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Title: AST Development for PEM Electrolyzers

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AST Development for PEM Electrolyzers

ASTWG Meeting 4th Meeting

Siddharth Komini Babu, Xiaoxiao Qiao, Abdurrahaman Yilmaz, Christopher Evan Van Pelt, Tanya Agarwal, Jacob Spendelow, Deborah Myers, David Cullen, Rangachary Mukundan

OUTLINE

- PEMWE ASTs
 - ASTWG Summary
 - Degradation test results
- Current PEMFC Component Specific ASTs
 - Catalyst AST, Carbon corrosion : Relation PEMWE anode AST
 - Membrane AST : Relation to PEMWE Membrane AST
 - GDL AST : Relation to PEMWE PTL AST
- Acknowledgements
- Conclusions

PEMEC ASTs

ASTWG Charter

- Recommend to the DOE: Protocols and targets related to PEM-Electrolyzer

<i>Electrolyzer Stack Goals by 2025</i>		
	LTE PEM	HTE
<i>Capital Cost</i>	\$100/kW	\$100/kW
<i>Electrical Efficiency (LHV)</i>	70% at 3 A/cm ²	98% at 1.5 A/cm ²
<i>Lifetime</i>	80,000 hr	60,000 hr

- Develop ASTs to predict 80,000 hours of life in desired application
- Develop additional ASTs to evaluate different PEM electrolyzer components

Specific goals:

- Develop a duty cycle representative of electrolyzer operation while capturing all degradation mechanisms
- Develop component specific ASTs to evaluate the durability of individual components in a reasonable time period (1 week to 1 month)

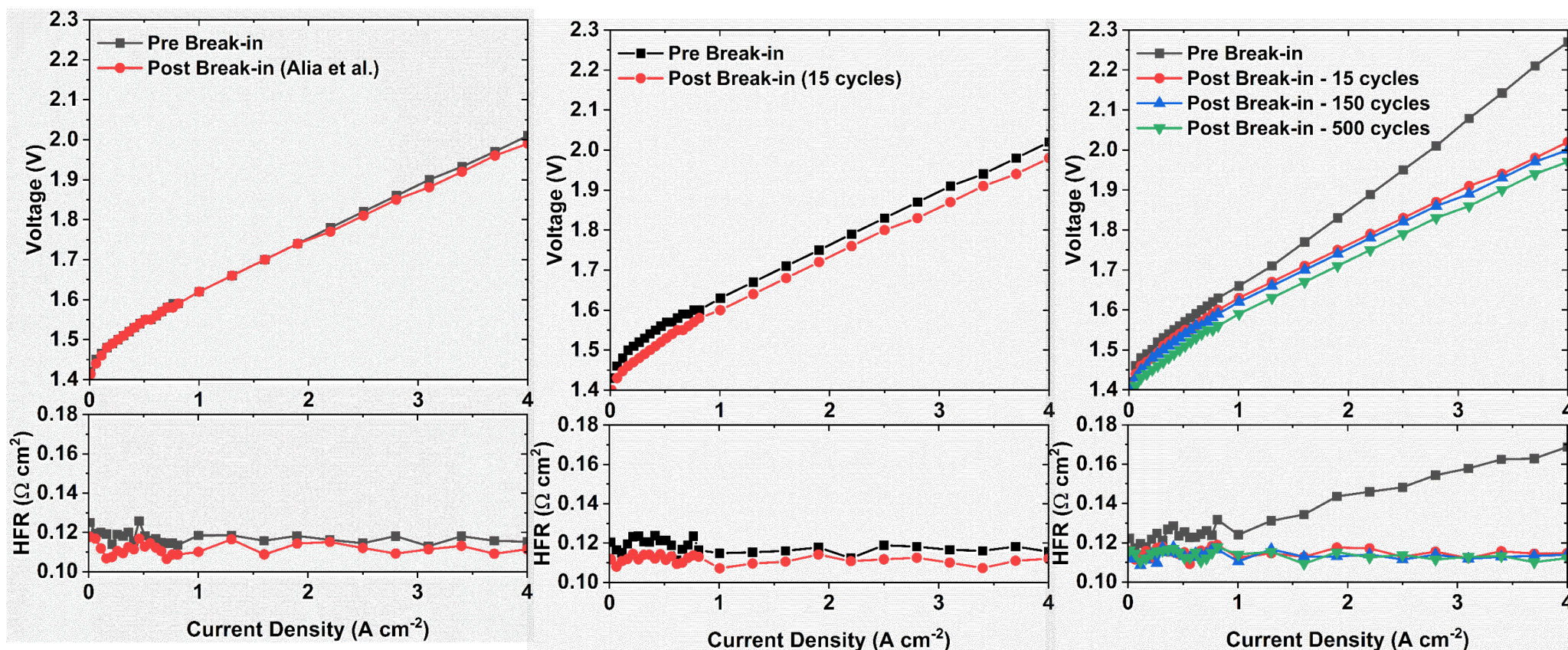
ASTWG Priority

Task Name										Average	Std Dev
Develop Electrolyzer Duty cycle that captures all relevant stressors at the MEA level	1	2	1	2	1	2	1	1		1.375	0.484
Anode Catalyst AST	2	1	2	1	2	3	2	2		1.875	0.599
PTL AST	3	4	4.5	3	4	4	5	4		3.9375	0.634
Membrane AST	4	3	3	4	3	1	4	3		3.125	0.927
Catalyst layer ionomer AST	5	6	6	6	5	7	3	6		5.5	1.118
Cathode Catalyst AST	6	10	7	5	6	6	6	5		6.375	1.494
Bi-polar plate AST	7	5	4.5	7	7	5	7	7		6.1875	1.058
Stressor Name											
Dynamic load cycling	1	4	1	2	7	2	1	3		2.625	1.932
Shut down/Start up. Allowing Ir/IrOx redox	2	1	4	1	1	1	2	6		2.25	1.713
High current operation (> 3A/cm2)	3	6	6	5	2	5	6.5	1		4.3125	1.919
High voltage operation (> 2.5V)	4	2	2	4	3	3	6.5	2		3.3125	1.434
Pressure cycling	5	5	5	7	5	4	4	7		5.25	1.089
Presence of contaminants (like Fe)	6	3	3	3	4	6	5	4		4.25	1.198
Hydrogen cross-over	7	7	7	6	6	7	2	5		5.875	1.615

ASTWG OEM Feedback

- Electrolyzers degrade very slowly and need to operate for long times
 - 7 to 10 year (up to 80,000 hour) operation
 - < 1% decay every 10,000 hours
 - Membrane failure (pinholes) more important than catalyst degradation
 - Need to develop 100x accelerated ASTs. Cannot use PEMFC developed ASTs
 - Thrifting precious metal loading will need anode catalyst AST
 - Thinner membranes will need membrane AST the take into account membrane mechanical properties in addition to chemical degradation
 - Lower cost PTL development will require a PTL ASTs
 - Stressors to take into account
 - Shutdown-Start up
 - Dynamic Load following
 - High pressure operation
 - High current operation
- MEA level AST should help predict impact of stack material changes and operating conditions on electrolyzer lifetime
- Component level ASTs should reflect same degradation mechanism for accelerated evaluation of new materials.

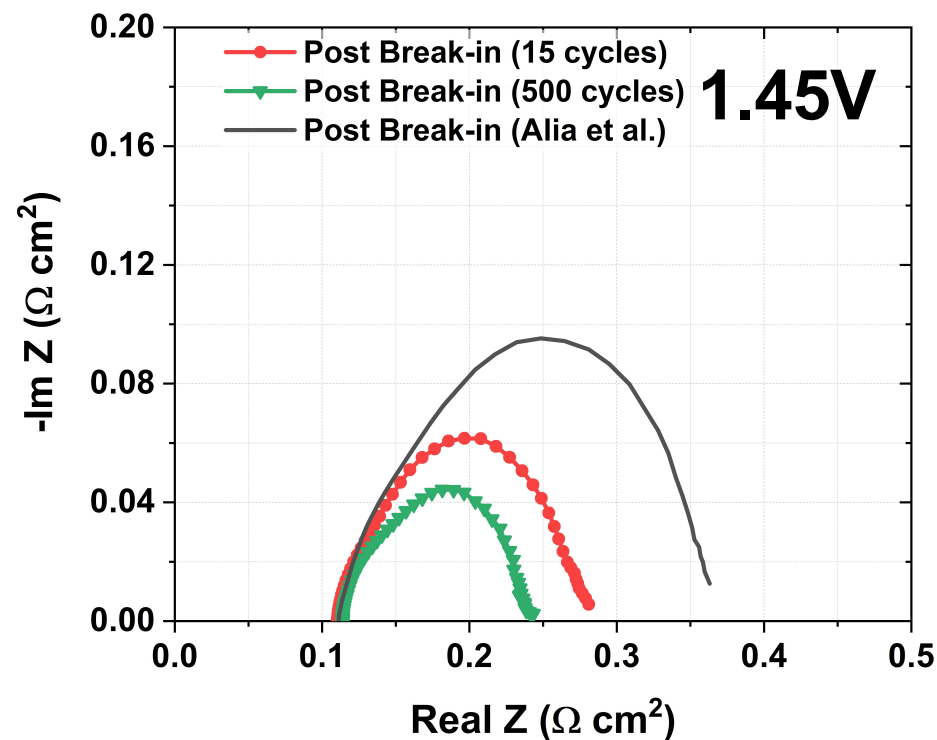
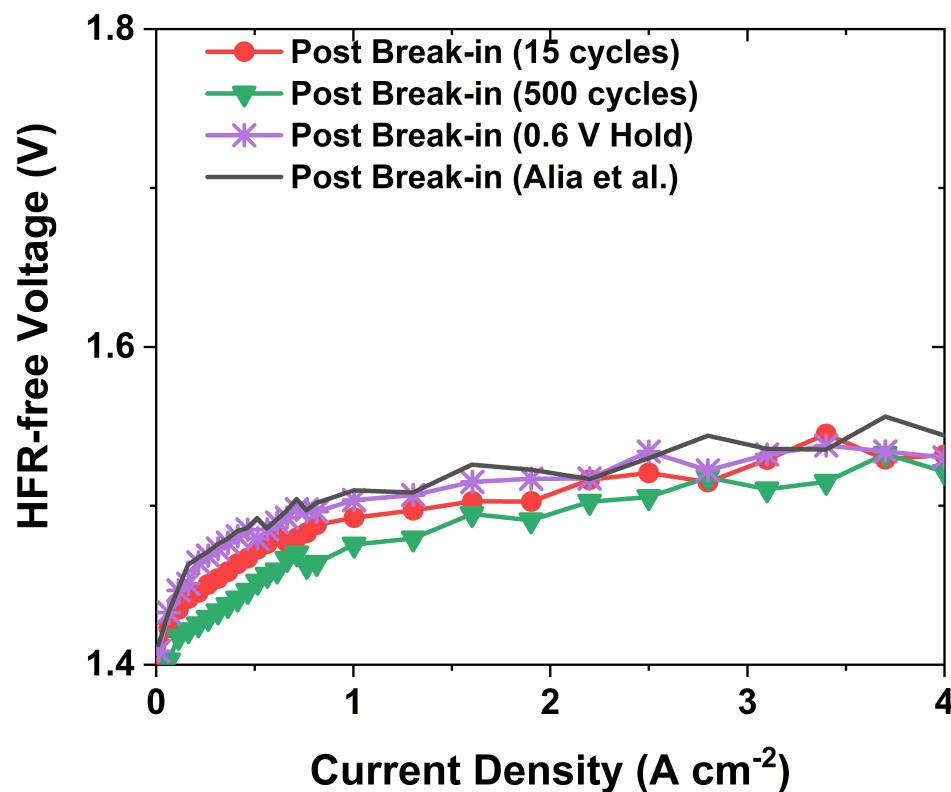
Break-in Protocol



S. M. Alia, S. Stariha, and R. L. Borup. "Electrolyzer durability at low catalyst loading and with dynamic operation." *Journal of the Electrochemical Society* 166.15 (2019): F1164.

New Break-in protocol being evaluated : Voltage cycling

Break-in Protocol



- New Break-in protocol results in improved anode kinetics with Alfa Aesar IrO₂ catalyst
- Being evaluated at NREL and needs to be proven in other catalysts

Sample Description

MEA Name	Membrane	Anode				Cathode				
			Loading					Loading		
		Catalyst	mg cm ⁻²	Ionomer	Ionomer Wt. %	Fabrication Method	Catalyst	mg cm ⁻²	Ionomer	I/C
LANL-H-210602-XQ-AST-MEA As prepared	N212	IrO2 (Alfa Aesar)	0.420	D2020	10	Rod coating				
LANL-H-210602-XQ-AST-210406-MEA01	N212 N211 N212	IrO2 (Alfa Aesar)	0.402	D2020	10	Spray coating	TEC10V50E	0.1	D2020	0.5
LANL-H-210602-XQ-AST-210413-MEA02	N212 N211 N212	IrO2 (Alfa Aesar)	0.402	D2020	10	Rod coating	TEC10V50E	0.098	D2020	0.5
LANL-H-210602-XQ-AST-210519-MEA05	N212 N211 N212	IrO2 (Alfa Aesar)	0.42	D2020	10	Rod coating	TEC10V50E	0.098	D2020	0.5
LANL-H-210602-XQ-AST-210520-MEA06	N212 N211 N212	IrO2 (Alfa Aesar)	0.40	D2020	10	Rod coating	TEC10V50E	0.096	D2020	0.5

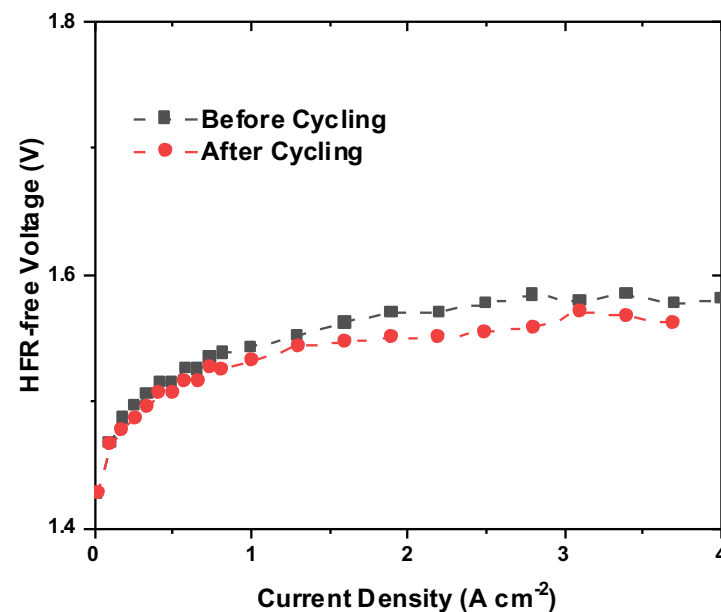
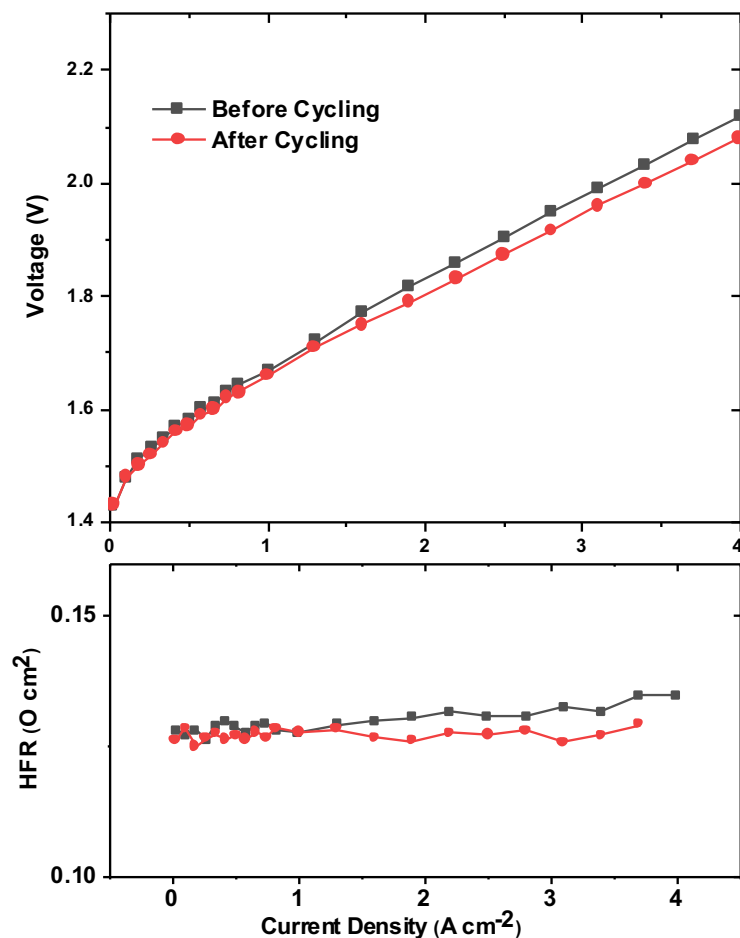
MEA Configuration

	IrO ₂ /Nafion 212
	Nafion 211
	Pt/C/Nafion 212

	Break-In Conditions	AST Methods	Characterizations	
MEA01	Shaun Alia's ECS paper	30000 potential cycles	TEM, EDX, XANE	EOL
MEA02	Shaun Alia's ECS paper	30000 potential cycles	TEM, EDX, XANE	EOL
MEA05	Shaun Alia's ECS paper	N/A	TEM, EDX, XANE	BOL
MEA06	LANL (500 cycles)	N/A	TEM, EDX, XANE	BOL

AST cycling (Literature conditioning)

MEA 2 : Rod-Coated, 10% ionomer loading



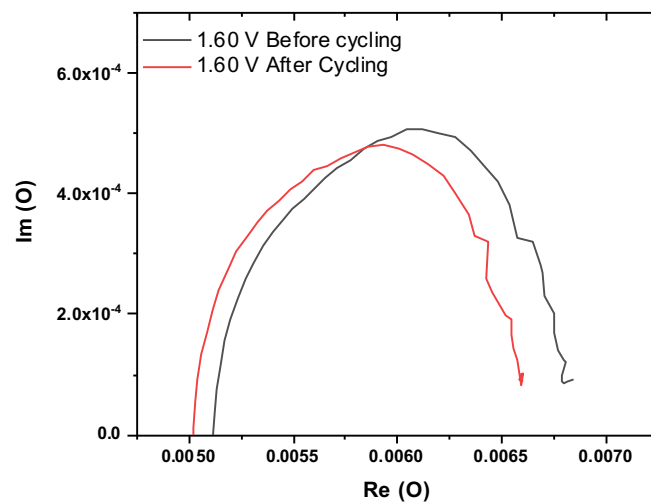
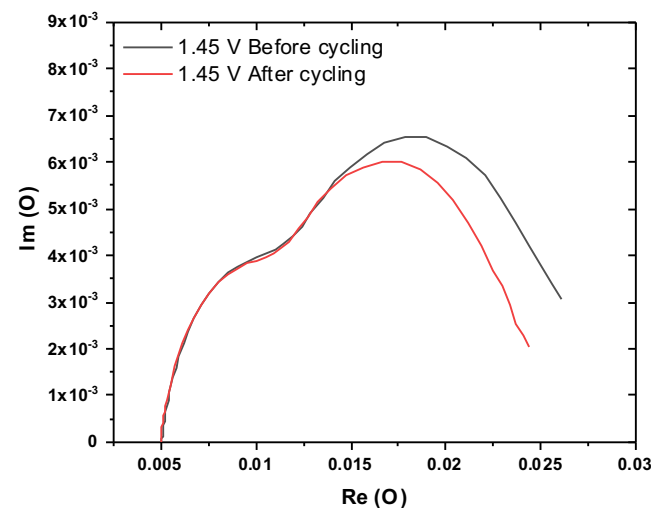
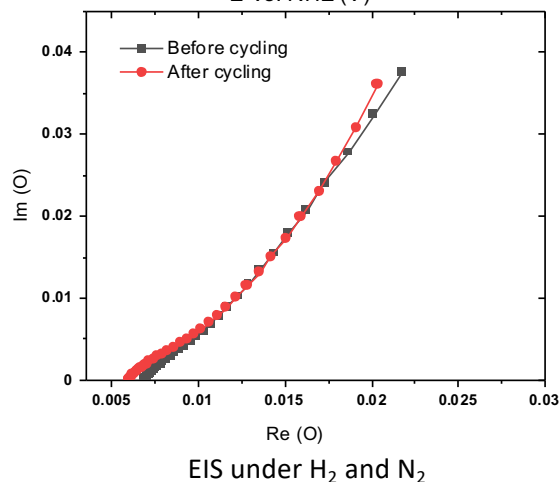
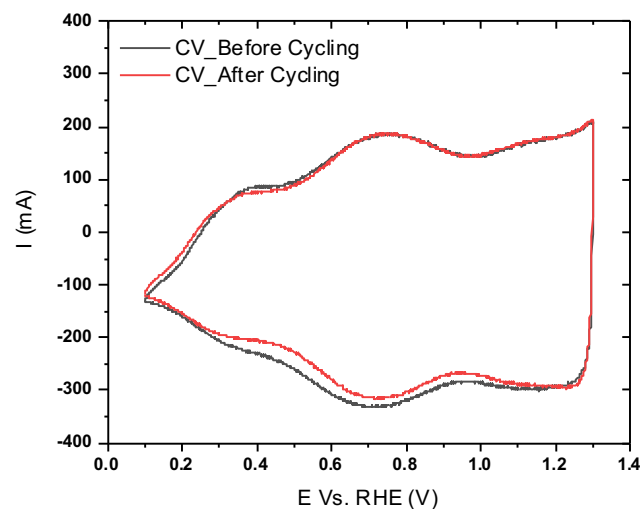
Break-in conditions: 1 hour hold at 0.2 A cm⁻², 1 hour hold at 1 A cm⁻², 30 min hold at 2 V, 2 h hold at 1.7 V, 30min hold at 2V.

AST conditions: 30,000 cycles of square-wave cycling between 1.45 V and 2 V.

Faster conditioning needs to be developed to better evaluate durability

Characterization during cycling

MEA 2: Rod-Coated, 10% ionomer loading

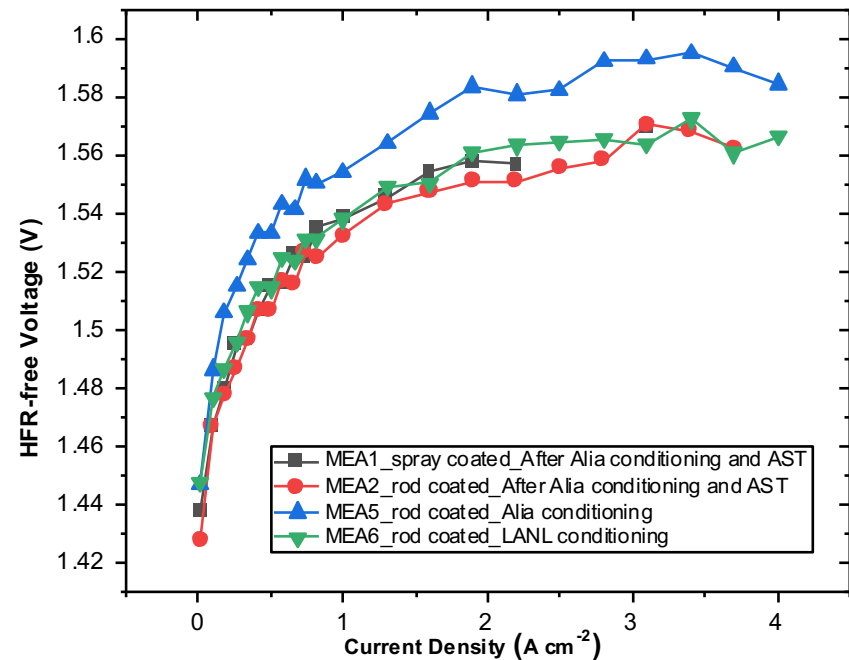
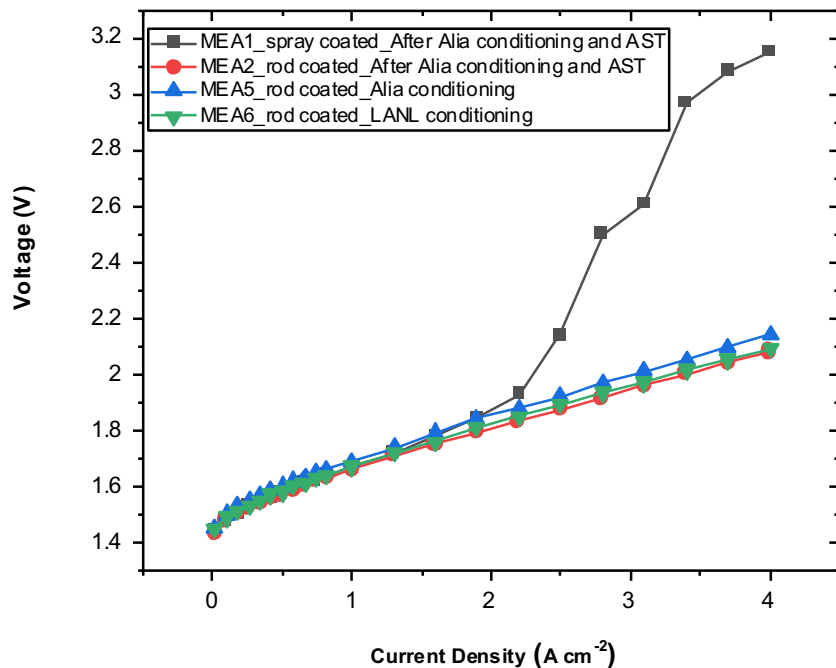


EIS can be used to track changes in the electrode. Pol curves are not so sensitive.

OER Kinetic resistance under Electrolyzer operation at constant potential of 1.45V

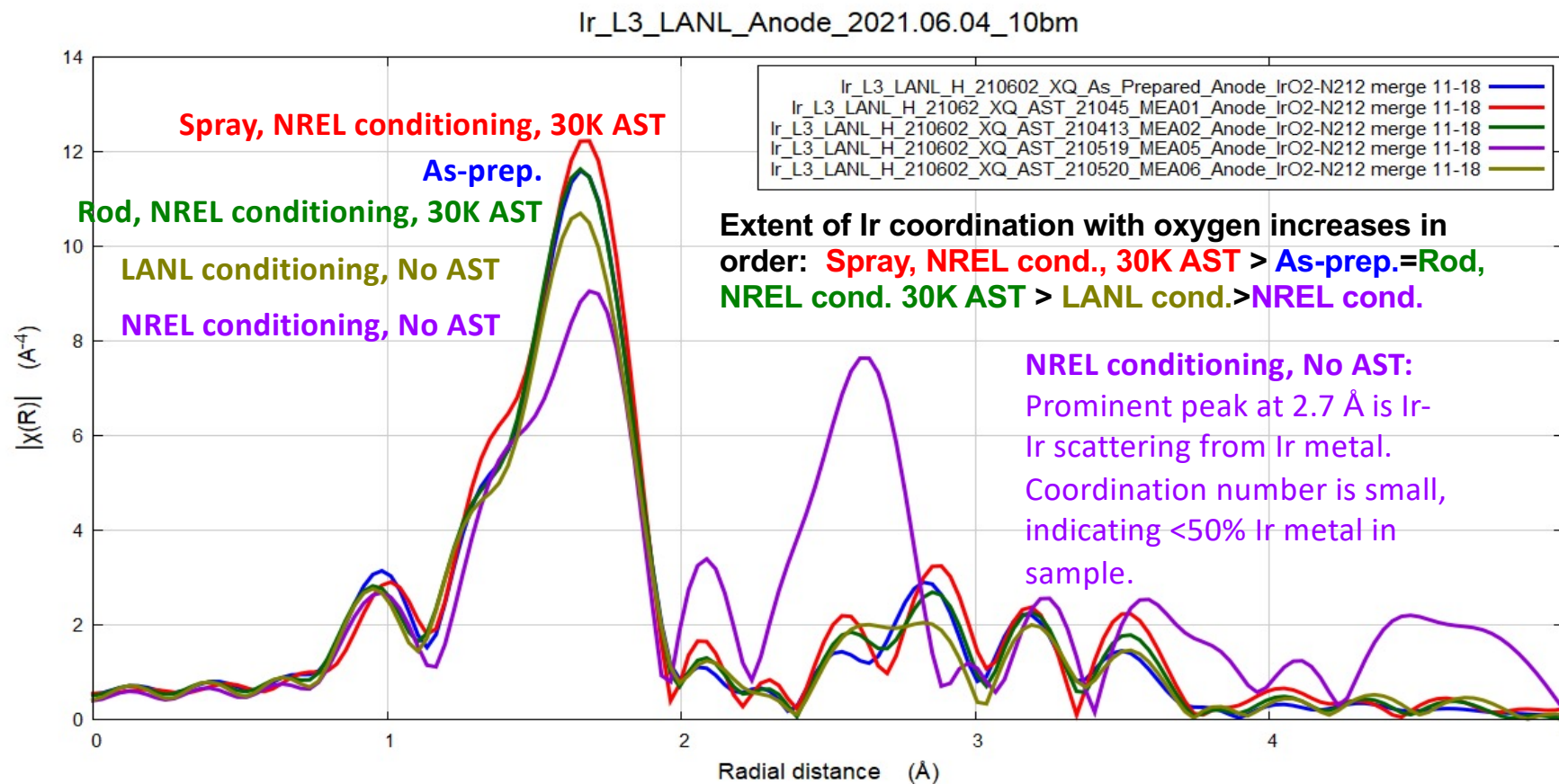
H₂/N₂ sheet resistance. Potential Ir incorporation into the ionomer.

Characterization during cycling

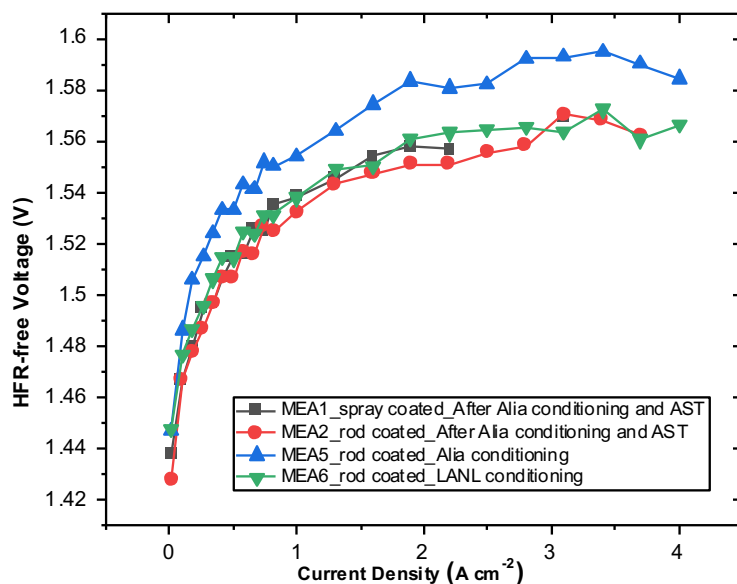


- All samples show little to no electrochemical degradation during the 30,000 cycle AST
- Amount of conditioning determines the kinetic performance
- Three layer spray coated MEA showed water transport problems at interface

EOT Characterization (APS)



EOT Characterization (APS)



Extent of Ir oxidation decreases in the following order:

NREL cond. Spray, 30K AST (MEA1)

As-prep = NREL cond. Rod, 30K AST (MEA2)

LANL cond. Rod (MEA6)

NREL cond. Rod (MEA5) (mix of oxide and metal)

Performance decreases in the following order:

NREL cond. Rod, 30K AST (MEA2)

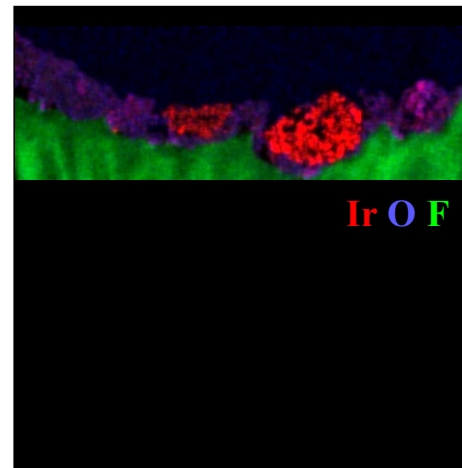
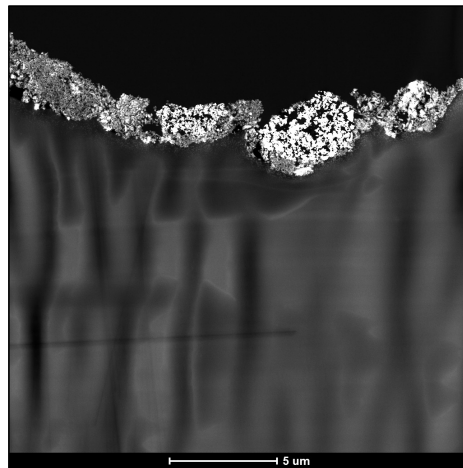
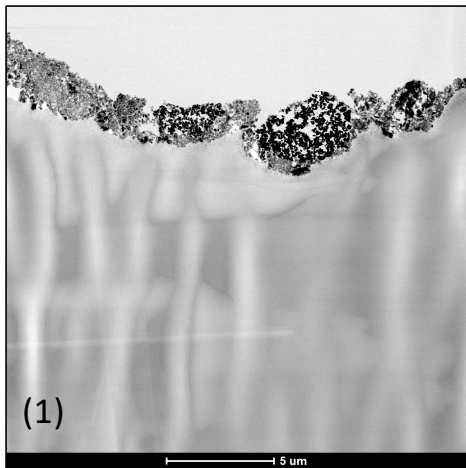
NREL cond. Spray, 30K AST (MEA1)

LANL cond. Rod (MEA6)

NREL cond. Rod (MEA5) (mix of oxide and metal)

EOT Characterization (ORNL)

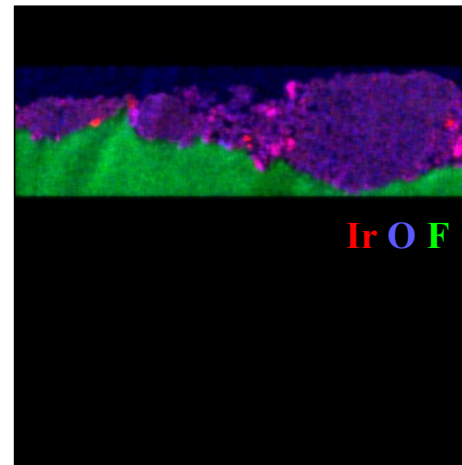
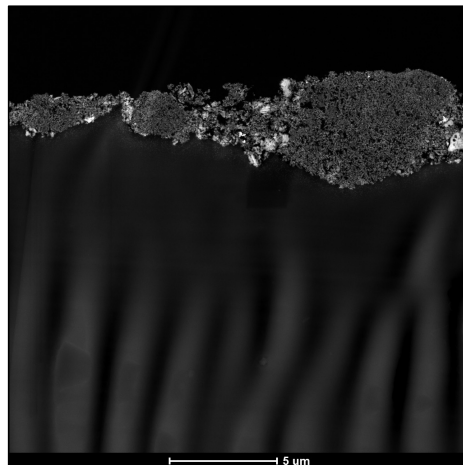
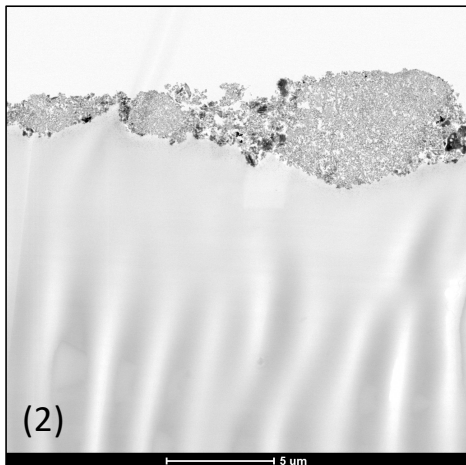
#5 anode



MEA #5 does have chunks of Ir metal in it

TEM (ORNL) data consistent with X-Ray (ANL) data

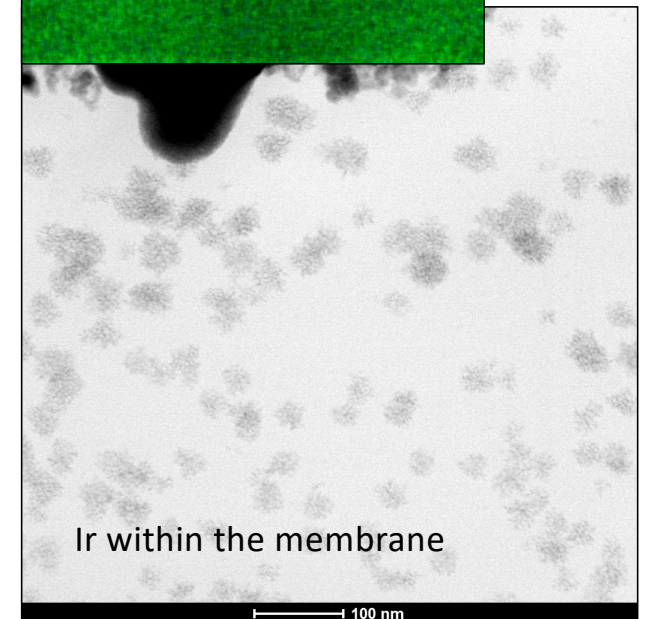
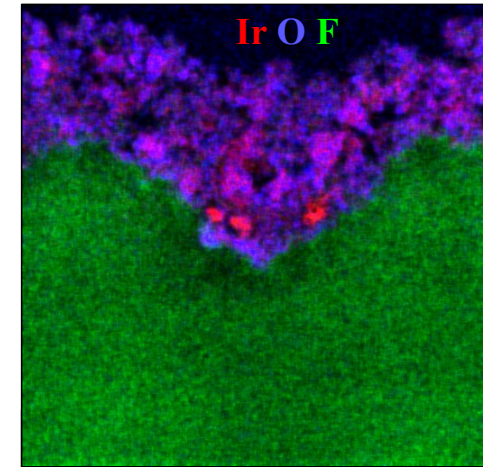
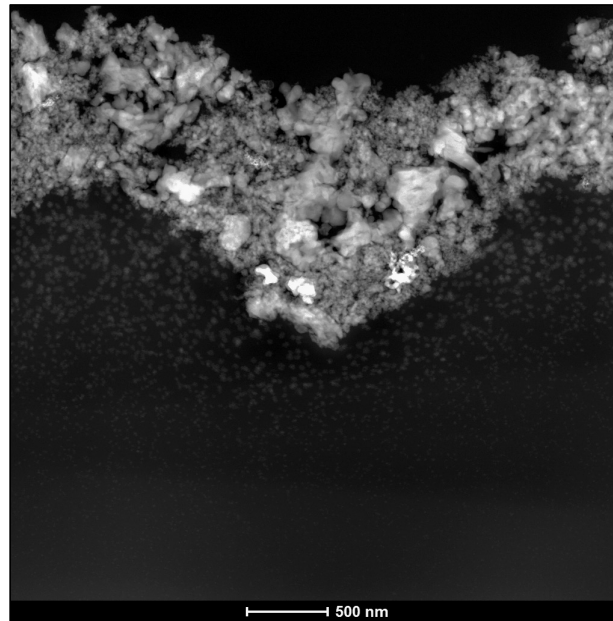
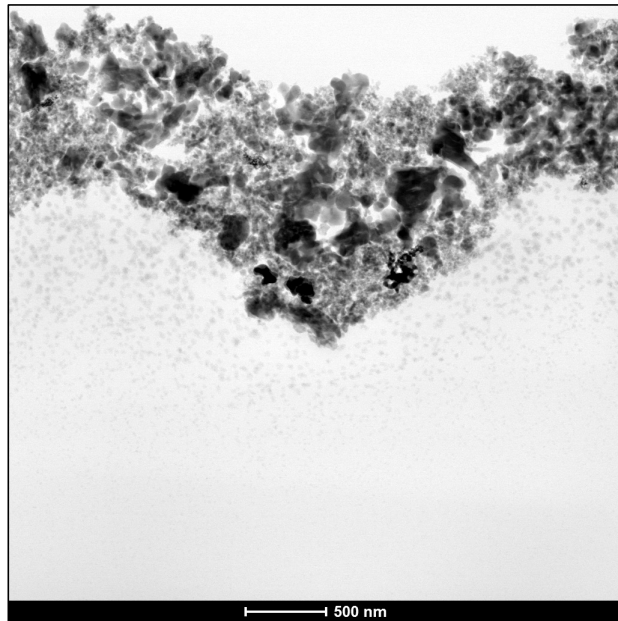
Alfa Aesar catalyst is a mixed Ir metal IrO₂ catalyst



MEAs with more Ir metal to start with have lower as prepared performance and take longer to condition

EOT Characterization (ORNL)

#5 anode



Ir particles observed in the membrane right next to the anode catalyst layer even after just conditioning the MEA

EOT Characterization (ORNL)

as-prepared

Spectrum	O	Ir
map 1	77	23
map 2	61	39
map 3	64	36
map 5	84	16
Mean value:	71	29
Sigma:	11	11

#1 anode

Spectrum	O	Ir
map 1	63	37
map 3	62	38
map 4	58	42
Mean value:	61	39
Sigma:	3	3

#2 anode

Spectrum	O	Ir
map 1	71	29
map 4	72	28
map 5	70	30
Mean value:	71	29
Sigma:	1	1

#5 anode

Spectrum	O	Ir
map 1	44	56
map 2	76	24
map 4	61	39
Mean value:	60	40
Sigma:	16	16

#6 anode

Spectrum	O	Ir
map 1	67	33
map 2	66	34
map 3	61	39
Mean value:	65	35
Sigma:	3	3

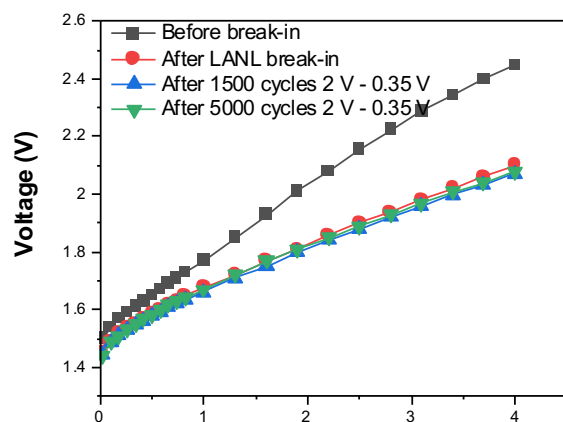
- Overview and EDS Quant of IrOx
- Ir(ox?) observed in membrane for all samples except as-prepped and #6
- Sample #5 has big chunks of Ir metal (>500nm)
- Trends in extent of oxidation hard to determine with EDS

Cycling to lower potential

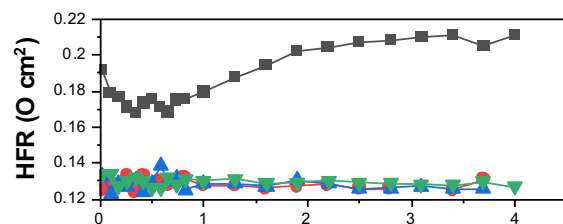
MEA 8: Rod-Coated, 10% ionomer loading, on N115 membrane

Cathode: 10V50E, spray coated, 0.1 mg/cm²

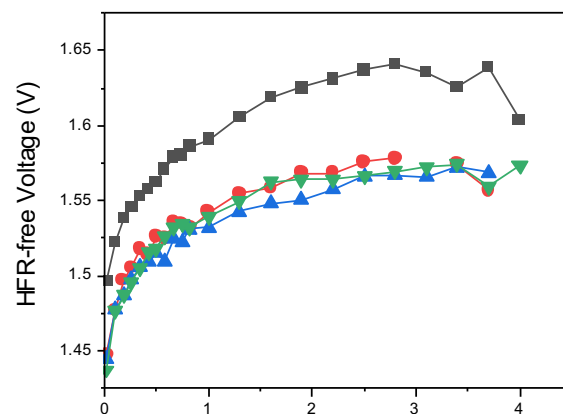
Anode: Alfa Aesa IrO₂, rod coated, 0.4 mg/cm²



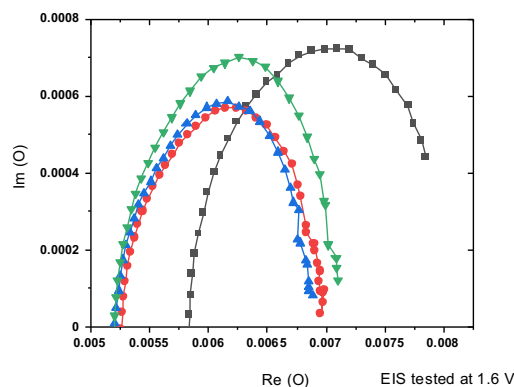
Current Density (A cm⁻²)



Current Density (A cm⁻²)

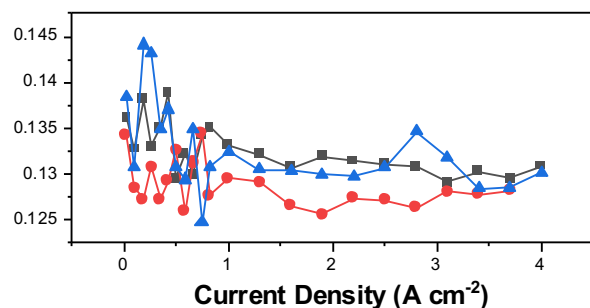
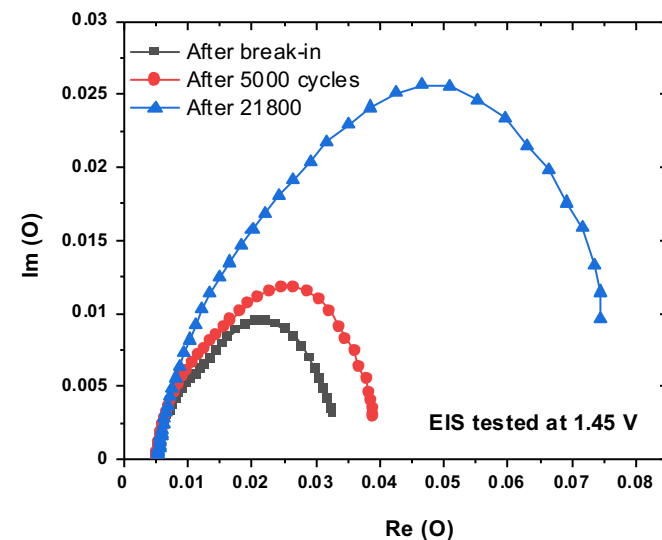
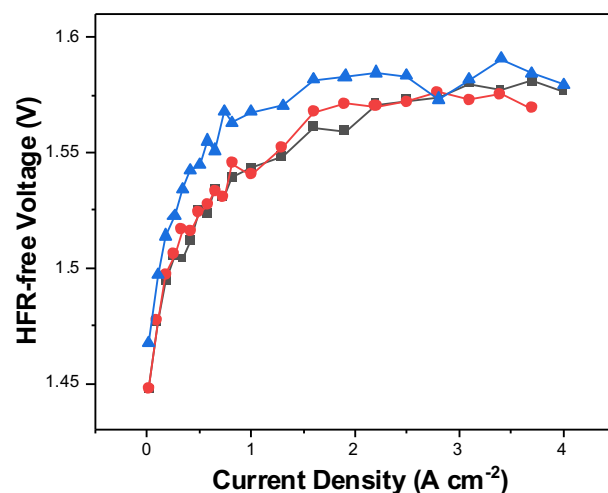
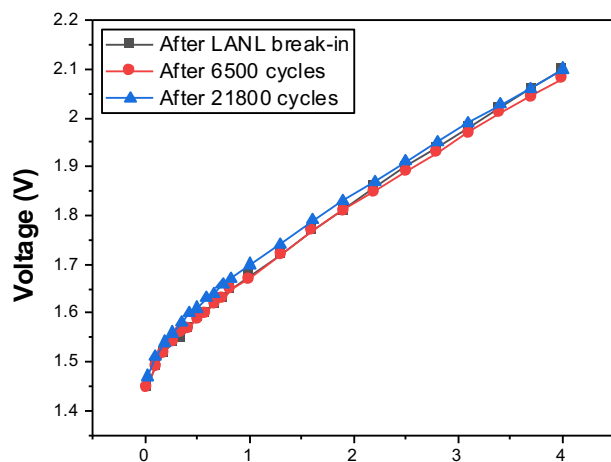


Current Density (A cm⁻²)



- Break in procedure leads to significantly improved performance
- N₂ used on the anode side to lower potential faster (if not wait times to reach 0.4V > 30 mins. Currently < 5 mins)
- Degradation observed in EIS even with just 5000 cycles (not reflected in pol curve)

Cycling to lower potential



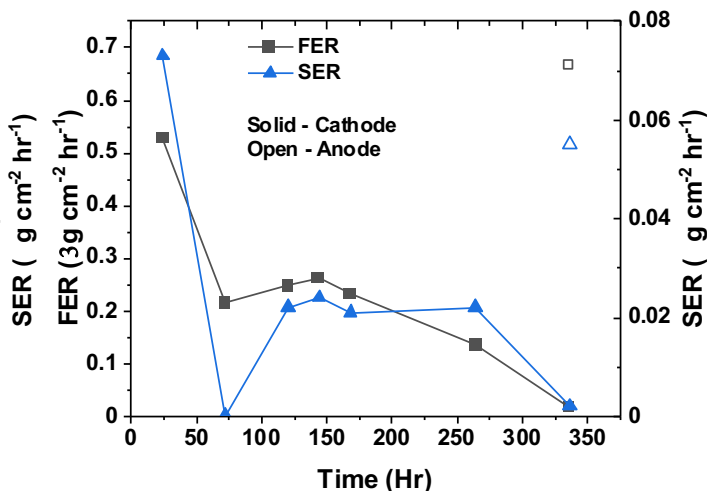
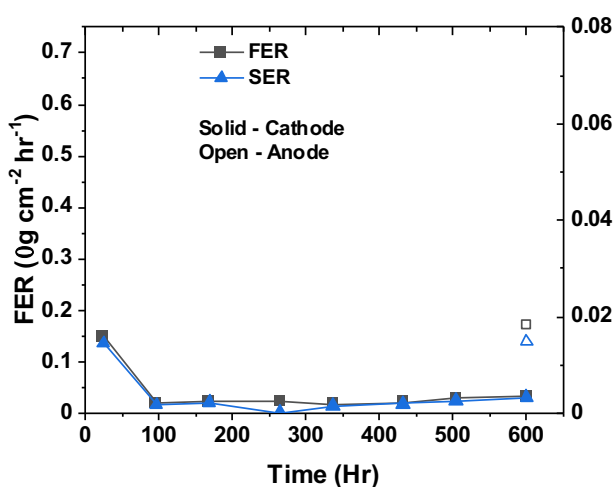
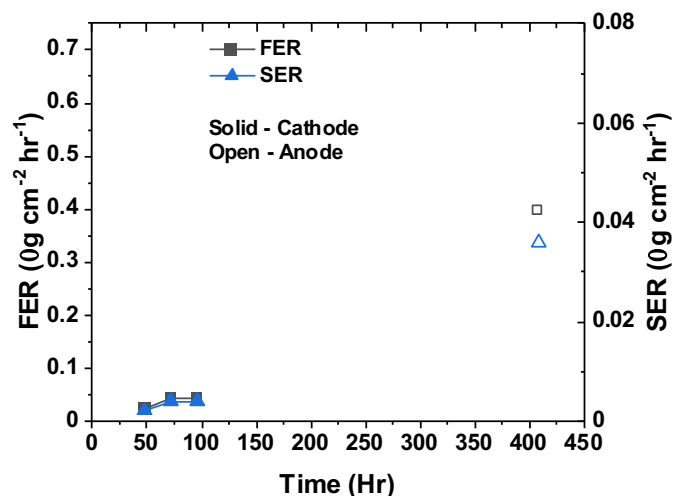
- Cycling to lower potential does yield greater degradation rates that previous 1.45 V to 2V cycling
- More cycles lead to performance change even with the 0.4 mg/cm² Ir loading

Membrane degradation

Membrane OCV AST

- OCV with H₂ (200 sccm)/ O₂ (200 sccm)+H₂O (25 cc/min)

	F	S		F	S
	$\mu\text{g cm}^{-2} \text{ hr}^{-1}$	$\mu\text{g cm}^{-2} \text{ hr}^{-1}$		$\mu\text{g cm}^{-2} \text{ hr}^{-1}$	$\mu\text{g cm}^{-2} \text{ hr}^{-1}$
				μm^{-1}	μm^{-1}
N212	0.398	0.036		0.00796	0.00072
N115	0.17	0.0149		0.00136	0.000119
N117	0.666	0.055		0.003806	0.000314

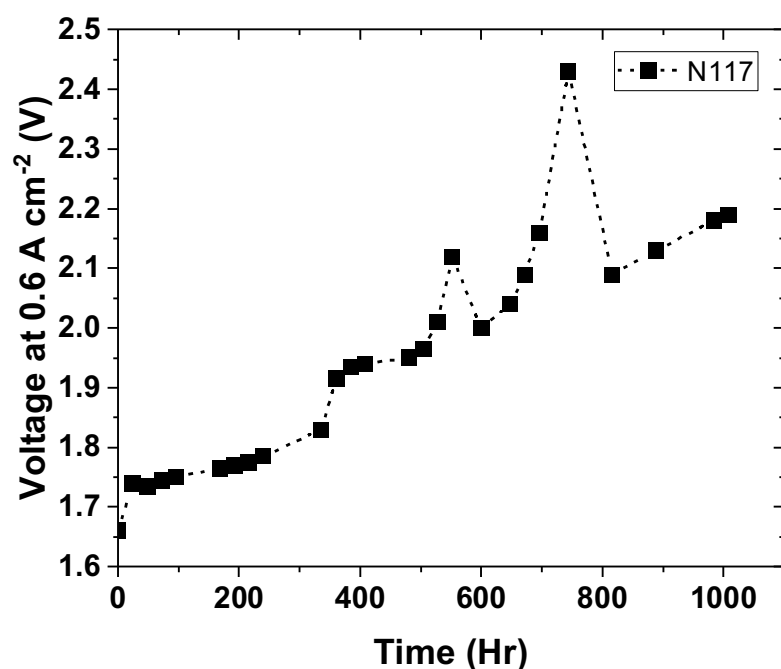


- Low FER corresponding to membrane degradation
- Comparable amounts in anode and cathode
- Increases with increasing fluoride inventory (increasing membrane thickness)
- Decreases with decreasing crossover

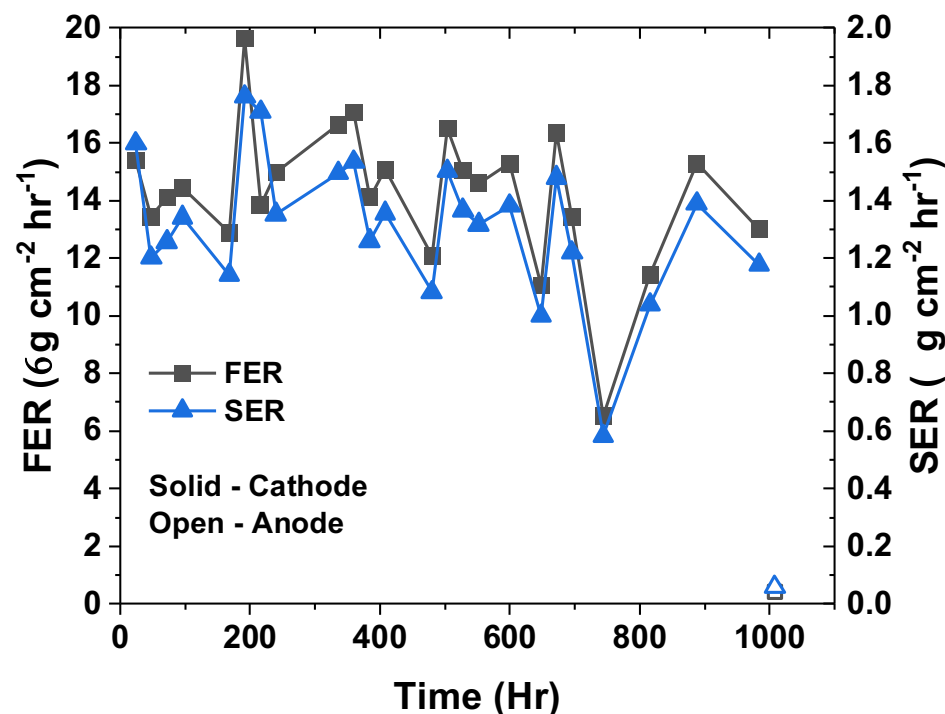
Membrane degradation

Membrane degradation electrolyzer

- 0.6 A/cm^2 with H_2O @ 25 cc/min



Significantly higher FER

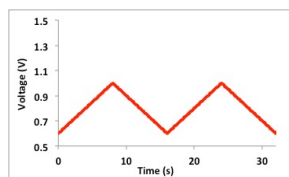


PEMFC Component Specific ASTs

Cathode electrocatalyst AST

0.6 to 1.0V cycles

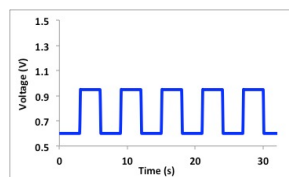
Triangle wave (50mv/s)



Target = 133 hours

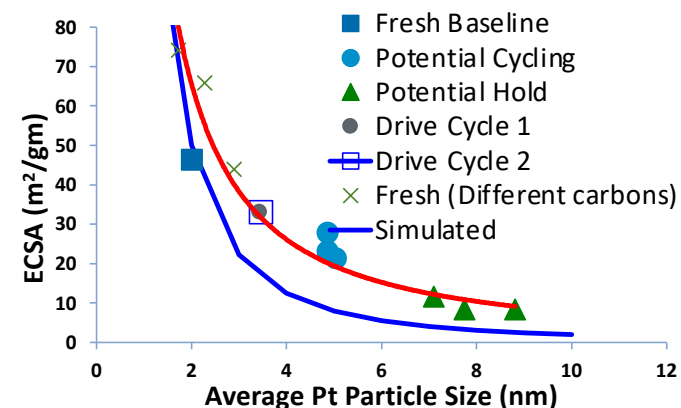
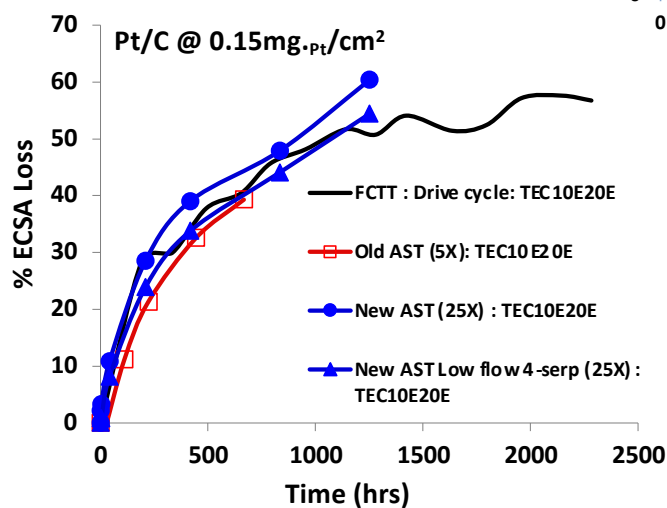
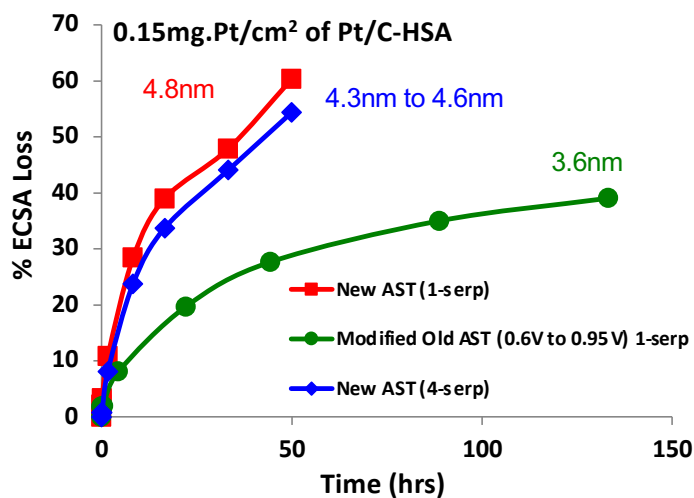
0.6 to 0.95V cycles

Trapezoid (0.5s rise time)

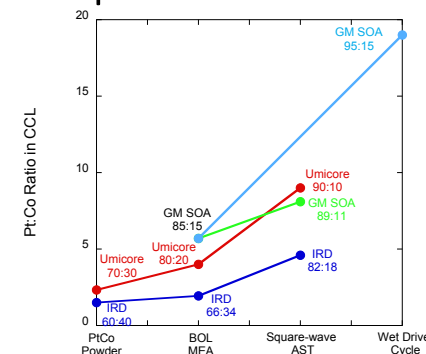


Target = 50 hours

New AST 5X faster than old AST and 25X faster than FCTT durability protocol



ECSA can be used as a surrogate to track particle size increase

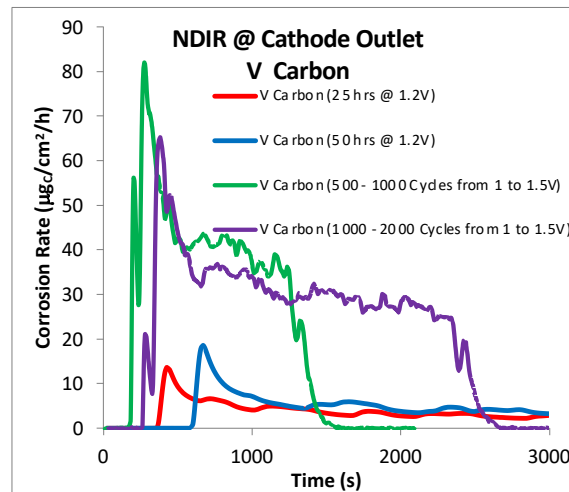
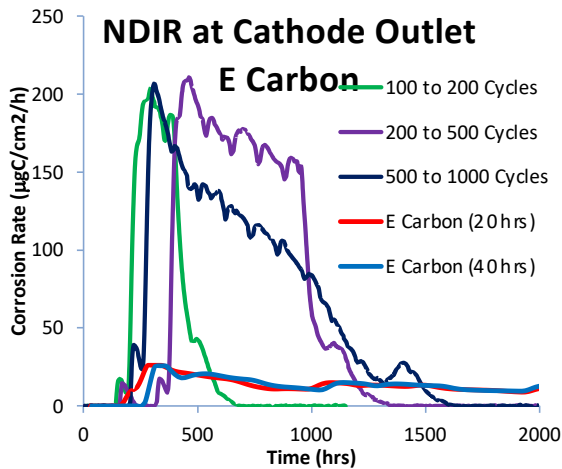
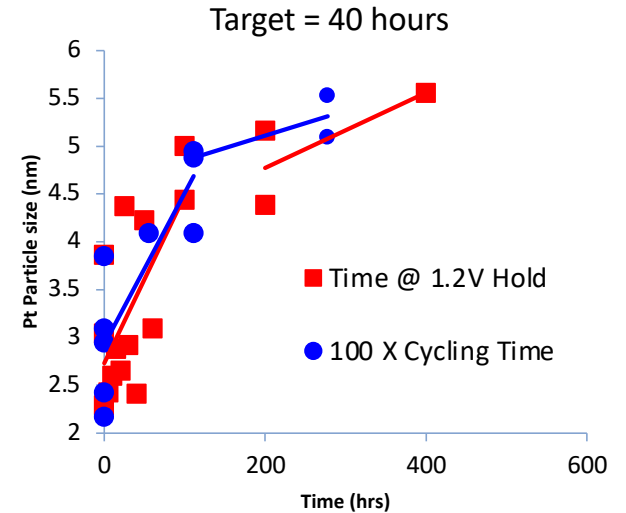
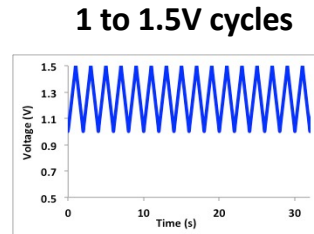
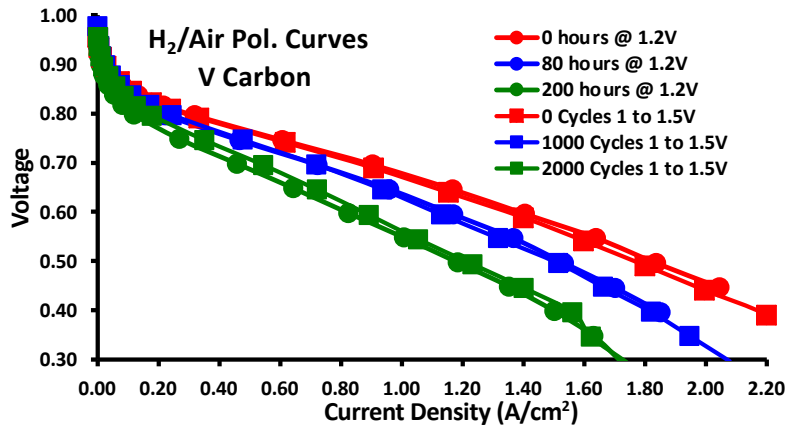


Mass activity can be used to track composition

https://energy.gov/sites/prod/files/2017/05/f34/fcto_myrrdd_fuel_cells.pdf

Carbon corrosion AST

Support AST

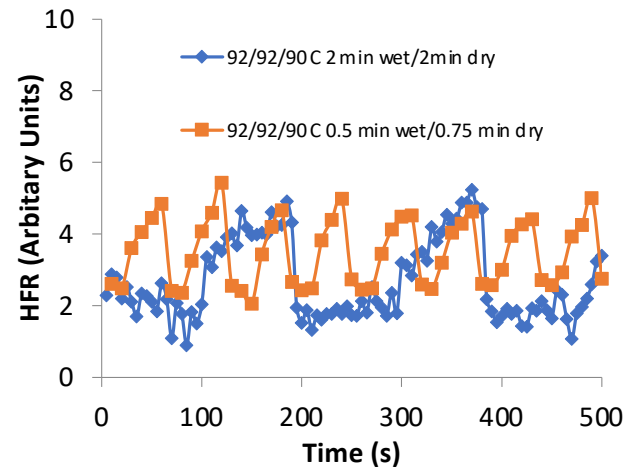
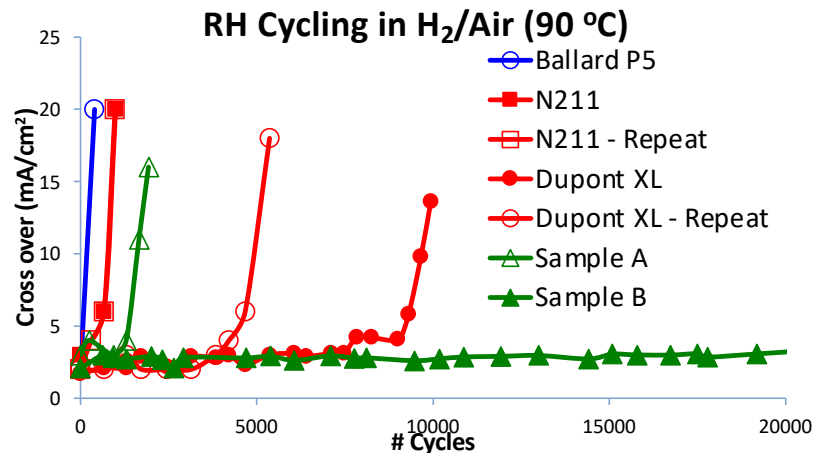
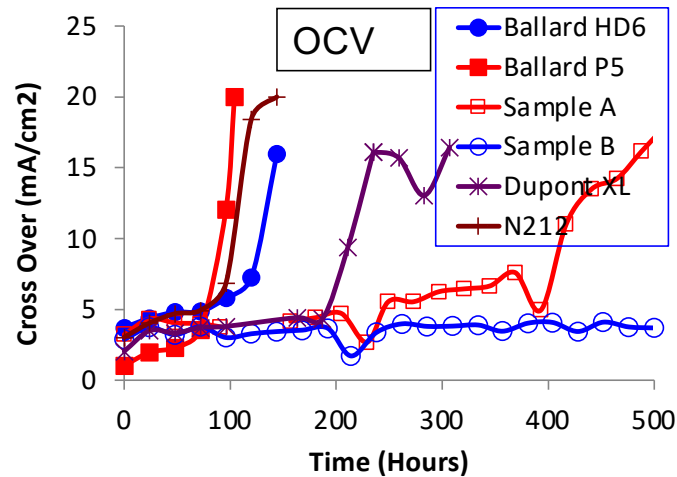
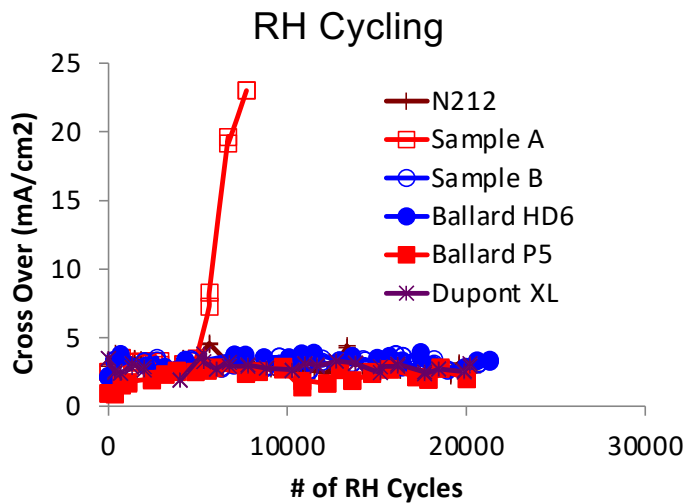


- ≈ 150 times faster decay in fuel cell performance
- ≈ 100 times faster Pt growth rate during cycling
- NDIR can be used to track corrosion

Relation to PEMWE Anode AST

- Potential cycling AST going between high current/potential and low potential using N_2 flow on the anode side to rapidly bring down anode potential $< 0.5V$
 - Will be the most accelerated AST, but is applicable only when electrolyzer is actually shut down and not switching between idle and full power.
- Potential cycling AST with LPL above 1.2V
 - Less accelerated but clearly see IrOx content increasing and Ir in the membrane and increased kinetic resistance at the lower loadings
- Potential cycling AST in H_2/N_2
 - Can do this test under low current conditions without access to an electrolyzer test stand and with just a potentiostat, gases and humidity bottles

Membrane AST



- RH cycling test does not have ability to distinguish between most PFSA membranes
- OCV shows ability to distinguish
- Fluoride emission is a good measure of membrane degradation (reported extensively in literature)
- Global membrane thinning associated with chemical degradation
- Combined mechanical/chemical AST further accelerates membrane degradation

Relation to PEMWE Membrane AST

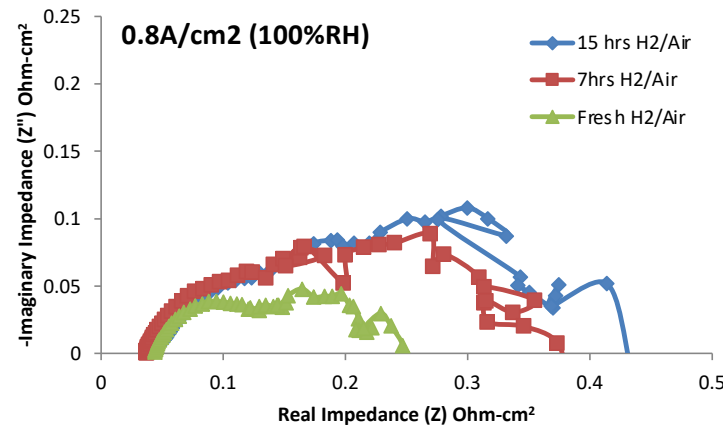
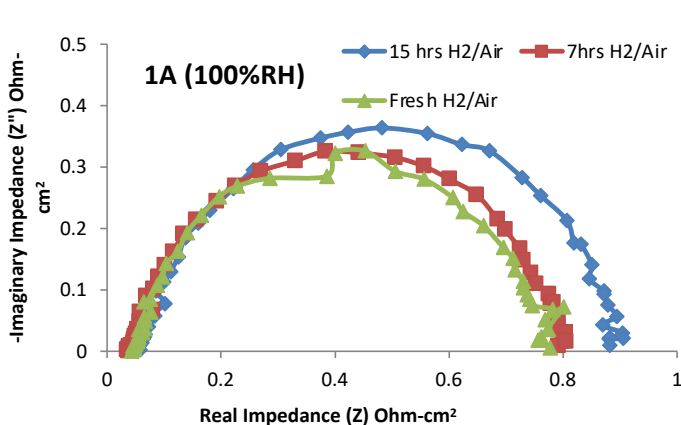
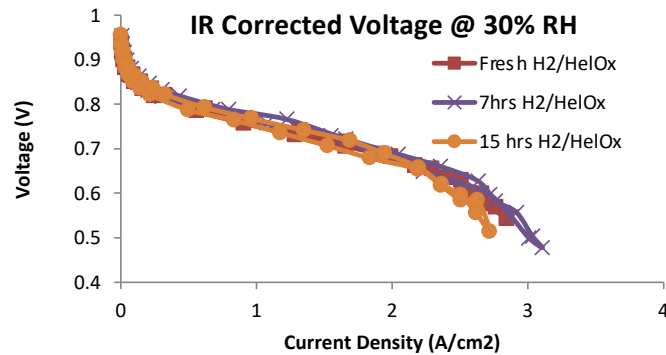
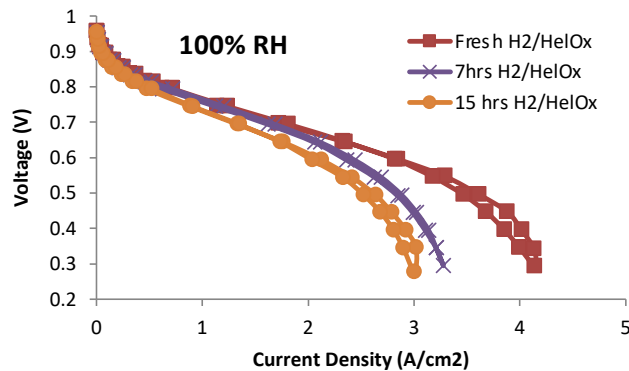
- Fluoride emission during electrolyzer operation (cathode) is observed and so the chemical degradation test can be used
 - Will have much greater acceleration factors than fuel cells
 - Acceleration factor will be critically dependent on membrane thickness and operating conditions
- Failure due to pinhole formation and pressure differential needs to be addressed.
 - RH cycling for mechanical stress may not be as relevant.
 - Pressure cycling needs to be accounted for
 - Asymmetric H₂O/Gas-pressure conditions in OCV mode (similar to combined Mech/Chem AST for fuel cells) can be developed for electrolyzer membrane AST. Example: High pressure H₂ on one side and O₂ on other with intermittent water injection

GDL AST

GDLs aged at 95°C in 30% H₂O₂

(Original procedure from Decode project, Peter Wilde: SGL Carbon)

Simulates loss of hydrophobicity and Substrate pore volume increase



- New/Aged GDLs show similar performance in low RH conditions
- Aged GDLs show lower high RH performance at high current density
- EIS shows higher mass transport resistance with aged GDLs
- XPS shows more surface oxidation of aged GDLs

R. Mukundan, J. R. Davey, K. Rau, D. A. Langlois, D. Spornjak, J. D. Fairweather, K. Artyushkova, R. Schweiss, and R. L. Borup, "Degradation of Gas Diffusion Layers in PEM fuel cells during drive cycle operation," *ECS Transactions*, **V58(1)**, pp. 919-926 (2013).

Relation to PEMWE Anode PTL AST

- MEA ageing will probably not work for a component specific PTL AST
 - Catalyst layer will also degrade under those same conditions
 - Might work for a very high loaded durable catalyst in combination with a defective PTL (limited use)
- Develop ex-situ test that simulates the oxidation behavior observed under electrolyzer conditions
 - Evaluate peroxide ageing as a component specific AST
 - Need to correlate with MEA data from Electrolyzers
 - Maybe develop this with uncoated PTLs and then extend to coated PTLs
 - Have to correlate both HFR increases (contact resistance/passivation) and hydrophobicity changes (water transport)

Acknowledgements

- H2NEW
 - LANL (Siddharth Komini Babu, Xiaoxiao Qiao and Jacob Spendelow)
 - NREL (Shaun Ali and Guido Bender)
 - ORNL (Dave Cullen)
 - ANL (Debbie Myers)
- Other LANL
 - Christopher Evan Van Pelt Tanya Agarwal, Abdurrahaman Yilmaz

Conclusions

- Electrolyzer duty cycle capturing all the relevant degradation modes needs to be developed
 - Currently using Idle (no current) and high power transitions. Will incorporate pressure gradients
- Component specific ASTs need to be developed and validated
 - Detailed mechanistic understanding and parametric study underway
 - Development of in-operando diagnostics to track degradation (EIS, crossover, fluoride emission)
 - Correlation with ex situ measurements (catalyst composition and particle sizes, Ir, Pt dissolution into ionomer/membrane, PTL contact resistance, hydrophobicity)
- Field validation
 - Future work under the ASTWG
- International collaboration
 - This meeting is a start
 - Bring potential international stake holders to harmonize AST protocols for electrolyzers

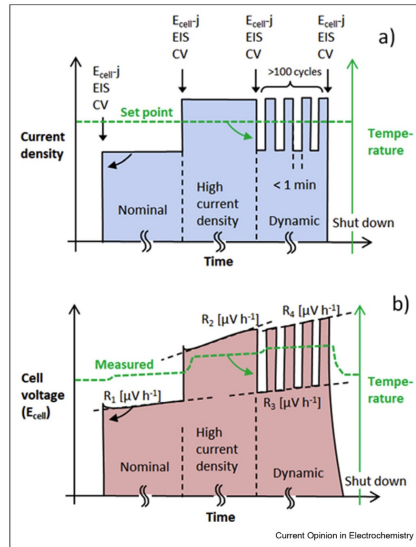
Backup Slides

Drive cycles and degradation

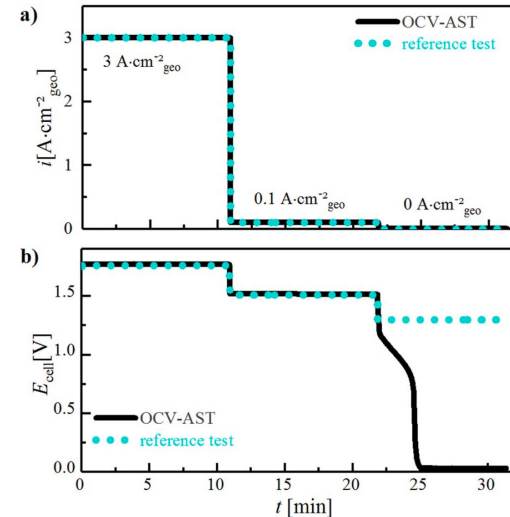
Next generation electrolyzer:

Follow load and not just full-power/idle mode

Meet cost and performance targets with lower catalyst loadings, thinner membranes, thinner PTL coatings etc.



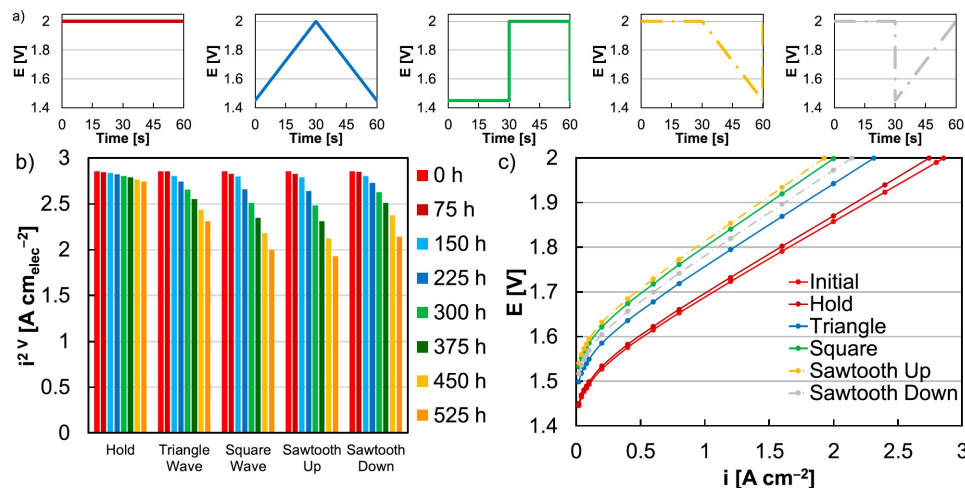
P. Aßman et al., *Current Opinion in Electrochemistry* 2020, 21:225–233



A. Weiß et al., *Journal of The Electrochemical Society*, **166** (8), 2019 F487-F497

- Need to develop catalyst specific ASTs that are relevant to load following applications
- Need to capture : Dynamic operation, high current operation, and shutdown

Catalyst ASTs



Developed fundamental understanding of degradation mechanisms leading to ASTs (electrocatalyst)

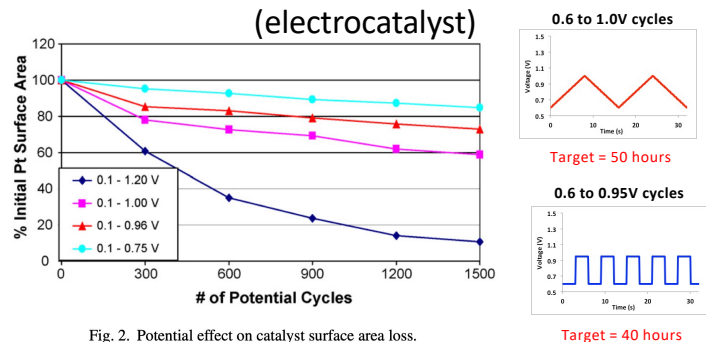


Fig. 2. Potential effect on catalyst surface area loss.

R.L. Borup et al., *Journal of Power Sources* 163 (2006) 76-81

Journal of The Electrochemical Society, 166 (15) F1164-F1172 (2019)

Systematic study of the effect of catalyst loading, and dynamic operation on electrolyzer durability

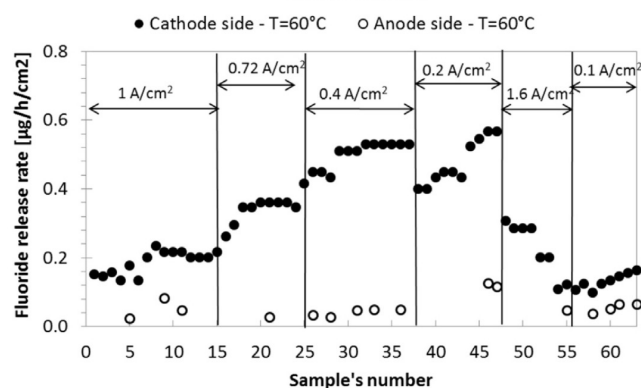
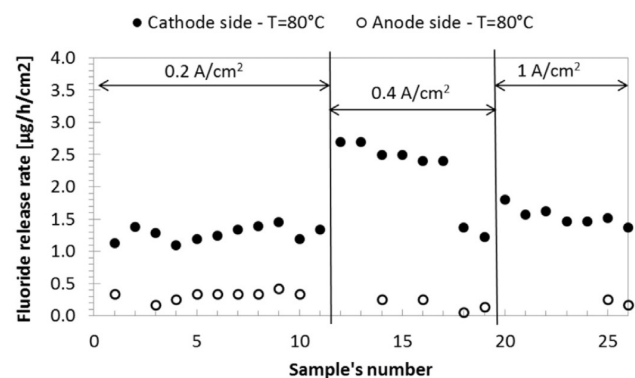
- Lower loadings and dynamic operation significantly accelerate degradation

- NREL has identified how various potential waveforms affect degradation at different catalyst loadings
- Better understand degradation mechanisms and perform parametric study
- Develop catalyst specific AST to rapidly evaluate state of the art unsupported IrOx anode catalyst and correlate to degradation observed in electrolyzer duty cycle

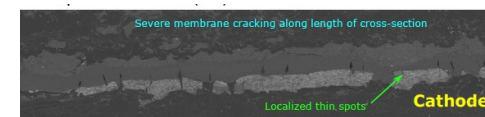
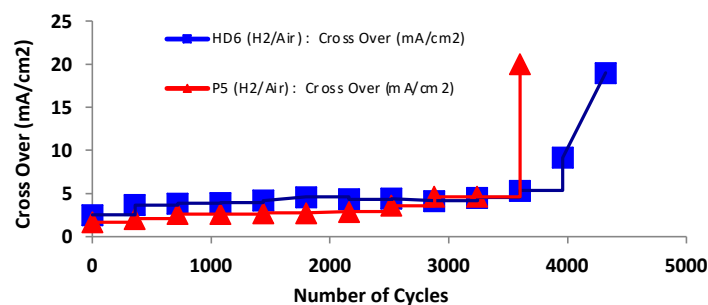
Membrane ASTs

Cathode side membrane degradation observed, accelerated by Temp and low currents

Previously developed combined chemical/mechanical ASTs based on correlation to field data (membrane) developed for fuel cells



M. Chandesris, Int. J. Hydrogen Energy, 40, 1353-1366 (2015)



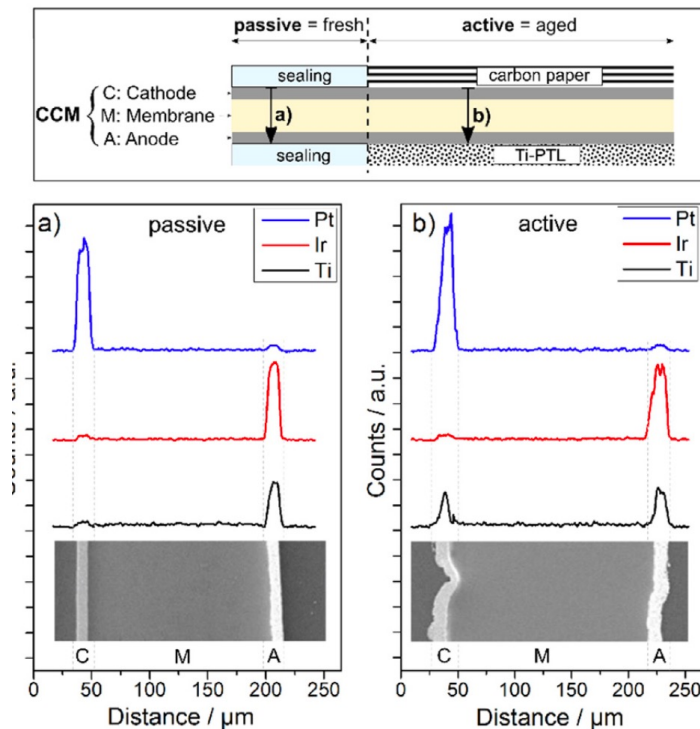
R. Mukundan et al., J. Electrochem. Soc., **165** (6), F3085-F3093 (2018)

- Evaluate influence of temp, current, partial pressure differential, shut-down/start up, and presence of Fe on membrane degradation
- Evaluate both fluoride emission rate and mechanical property changes during drive cycle experiments
- Develop membrane specific AST

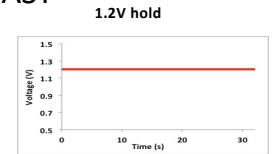
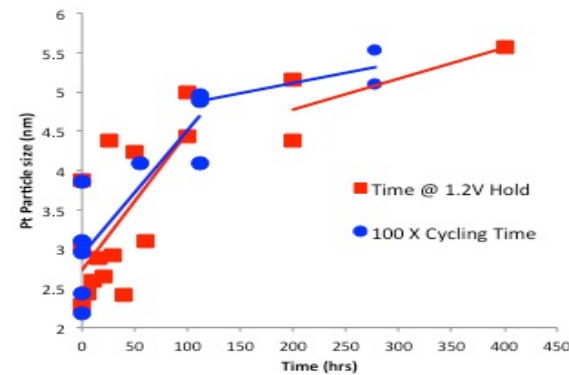
PTL ASTs

Ti leaching from un-coated PTLs is a significant source of degradation: Contact resistance increase and poisoning of anode catalyst

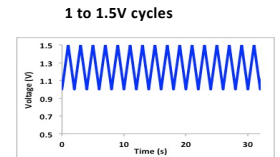
Have developed catalyst support AST with 100X acceleration factor over previous AST



C. Rakousky et al, J. Power Sources. 326, 120-128(2016)



Target = 400 hours



Target = 40 hours

N. Macauley et al., J. Electrochem. Soc., **165** (6), F3148-F3160 (2018)

- Evaluate corrosion rates (leaching rates and oxidation rates) of coated and un coated PTLs under different conditions
 - Temperature
 - Potential/current density
 - Track contact resistance and water transport
- Develop PTL specific AST

AST development (Literature)

liten
cel2tech

Analytical Methods and main outcomes

AST-1: 48h AST signal @ 90°C repeated at least 4 times



- 3 A/cm² ($E > 2V$) : speed up BP corrosion
- 0,3 A/cm² : speed up membrane attack

AST-2: 48 h AST@ 90°C repeated at least 4 times



- Longer step time at low current density to amplify the membrane chemical attack

AST-3: 48 h AST@ 90°C repeated at least 4 times

with ΔP ($P_{O_2} = 4 \text{ bar}$ vs. $P_{H_2} = 1 \text{ bar}$)



- Suppose to amplify the oxygen permeation and accelerate the membrane attack

AST-4: 48 h AST@ 90°C repeated at least 4 times with 5ppm Fe ions



- Adding metal ion impurities may catalyse the Fenton reaction.

Dynamic operation results in 40X faster degradation rate than steady state hold

AST -2 demonstrates high degradation rates

AST -4 Need to evaluate with ppb levels of Iron ($\mu\text{g}/\text{cm}^2$) in membrane can result in accelerated degradation

AST development (Literature)

Na Li, Samuel Simon, ArayaSøren, and Knudsen Kær, Electrochimica Acta 370 (2021) 137748

Table 1
Examples of AST strategies used in PEM water electrolysis.

Stressor	AST strategy	Failure mode	Reference
High current density	4 A cm ⁻² for more than 750 h	Anode catalyst degradation (Ir leaches out)	[9]
Dynamic load cycling	0 A cm ⁻² - 2A cm ⁻² , dwell time of 100 s, 60 s and 10 s for each test	Fluoride emission with fast load switches	[16]
OCV-AST (dynamic load cycling)	3 A cm ⁻² for about 10 min, 0.1 A cm ⁻² for about 10 min and an OCV for about 10 min	Passivation of Ti-PTL and hydrous iridium oxide	[8]
On/off (dynamic load cycling)	0 - 1 A cm ⁻² for 5500 h	Catalyst layer corrosion and membrane thinning	[30]
Low load cycling	0 A cm ⁻² - 0.5 A cm ⁻²	Charge transfer losses especially on the hydrogen side	Current work
High load cycling	1.2 A cm ⁻² - 2 A cm ⁻²	Membrane thinning and catalyst degradation	Current work